Structural modulations in $Sr_{14}Cu_{24}O_{41}$ and their relation to charge ordering

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Structural properties of the spin chain and ladder compound $Sr_{14}Cu_{24}O_{41}$ have been studied using diffraction with hard x-rays. Strong incommensurate modulation reflections are observed due to the lattice mismatch of the chain and ladder structure, respectively. While modulation reflections of low orders display only a weak temperature independence, higher orders dramatically increase in intensity when cooling the sample to 10 K. All observed modulation reflections are indexed within the super space group symmetry and no structural phase transition could be identified between 10 K and room temperature. We argue that these modulation reflections are not caused by a five-fold periodicity of the chain lattice, as claimed by Fukuda *et al.* Phys. Rev. B **66**, 012104 (2002), but that holes localize in the potential given by the lattice modulation, which in turn gives rise to a further deformation of the lattice.

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I. INTRODUCTION

In high-temperature superconductors the correlation of spin and charge play a dominant role for the formation of the superconducting state. Probing the ordering and dynamics of these degrees of freedom in materials that exhibit a different dimensionality might give further insights into the superconducting mechanism. In spin chain and ladder materials the basic structural unit is similar to the one of high-T_c superconductors. While in the superconductors CuO_2 plaquettes form a two-dimensional network, in ladder and chain materials they compose one-dimensional arrays. $Sr_{14-x}Ca_xCu_{24}O_{41}$ is a family of materials that exhibits both CuO_2 chains and two-leg Cu_2O_3 ladders that are stacked in subsequent layers along the crystal *b*-axis. They are particular exciting since they also show superconductivity for x=11.5 under an external pressure of 3 GPa [1], which was theoretically predicted [2, 3].

The average valence state of Cu in the $x = 0$ material is 2.25. However, optical conductivity and x-ray absorption measurements at room temperature have shown that out of the 6 holes per formula unit five are located on chain sites and about one hole resides on a ladder site [4, 5]. On the other hand more recent NMR experiments are explained in terms of a transfer of holes from the ladders into the chains with decreasing temperature [6]. The insulating character indicates that the holes are localized at low temperatures and indeed a charge valence ordering below 200 K is claimed on the basis of results obtained by many different experimental techniques [7, 8, 9, 10, 11, 12]. The existence of two different Cu sites in the chains has been shown by NMR measurements were two distinct resonances have been observed [7]. These are assigned to two different hole sites, i.e. one located in between two Cu spins S=1/2 forming a dimer, the other one belonging to the holes which decouple the dimers from each other. Above 200 K the split peak merges into a single peak due to thermal fluctuations. The magnetic susceptibility only slightly decreases at the charge ordering temperature of about 200 K, but dramatically decreases below 80 K indicating the formation of spin dimers. By inelastic neutron scattering experiments a spin gap of 14 meV in the chains with a fivefold dispersion was observed [8, 9]. A model that explains both the magnetization and the dispersion is that two Cu spins separated by a Zhang-Rice singlet form a dimer and two dimers are separated by another two Zhang-Rice singlets, such that the overall periodicity of the chains is five times enlarged [9]. The hole localization also couples to the lattice as shown by thermal expansion experiments [10]. Two x-ray studies aimed to detect the structural distortion due to a hole localization come to different conclusions. Cox *et al.* identify superlattice reflections at (0, 0, 1.25) and (0, 0, 1.5) which are attributed to a quadrupling of the basic chain unit cell due to charge order. These superlattice reflections disappear at about 300 K. Furthermore they find a diminishing intensity of the (0, 0, 2) Bragg reflection which is explained by a sliding of neighboring chains along the c-axis [13]. In contrast, Fukuda *et al.* report a five-fold superstructure based on the observation of superlattice peaks at (0, 0, 2.2), (0, 0, 3.8) and (0, 0, 4.8). These peaks show only a weak temperature dependence and are stable up to high temperatures [14]. In both investigations the superlattice reflections have been ascribed solely to the structural properties of the chains.

We have characterized a single crystal of $Sr_{14}Cu_{24}O_{41}$ with high energy x-ray diffraction. At room temperature we find a strong incommensurate modulation of both chains and ladders due to their different *c*-axis lattice parameters. Decreasing the temperature to 10 K, additional reflections appear that are well described within the super space group symmetry. We identify a continuous transition of the modulation shape from a sinusoidal

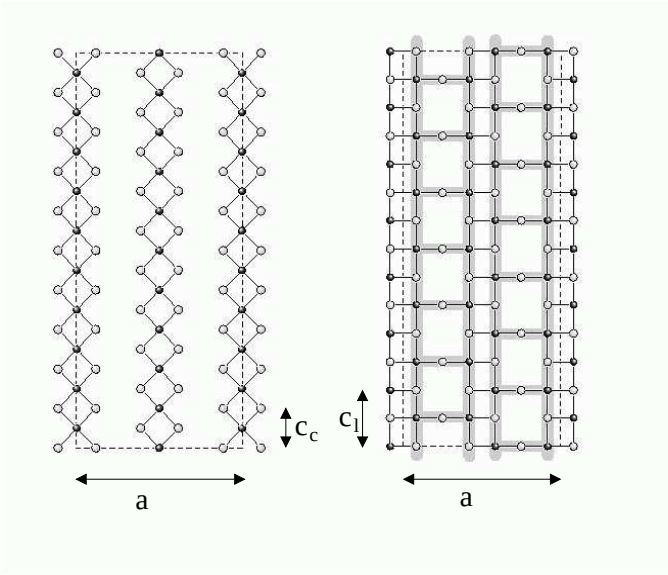

FIG. 1: Sketch of the chain (left) and ladder (right) structure. The filled points represent copper, the open circles oxygen. The Sr-layer is not shown.

shape to a modulation that involves various higher order Fourier components. The origin for the variation of the distortion shape at low temperatures is attributed to charge localization.

II. EXPERIMENTAL DETAILS

The sample was grown by the traveling solvent floating zone method [15, 16]. A piece of $3 \times 0.5 \times 2$ mm^3 size was cleaved out of the wafer and no further surface preparation was applied. The experiment was performed at the high energy beamline BW5 at HASYLAB in Hamburg [17]. The large penetration depth of the 100 keV x-ray beam into the sample of about 2 mm assures that only bulk properties of the sample are probed. A SiGe gradient crystal [18] was chosen for monochromator and analyzer with a convoluted full width at half maximum (FWHM) of about 40", resulting in a longitudinal resolution of 0.012 Å^{-1} (FWHM) at the (0, 0, 2) ladder reflection. The high perfection of the sample mosaic of 0.005° gives a transverse resolution of 5×10^{-4} Å^{-1}. The sample was mounted in the *bc*-scattering plane on the cold head of a closed cycle cryostat with a temperature stability of better than 0.2 K.

III. RESULTS

A. Structural considerations

The structure of $Sr_{14}Cu_{24}O_{41}$ can be described as alternating layers of ladders and chains, sketched in figure 1. The ladders have a composition of Sr-Cu_2O_3-Sr with an orthorhombic unit cell of Fmmm symmetry and lattice parameters of a=11.47 Å, b=13.41 Å and c_l=3.926 Å. The chains are CuO_2 units with identical values of a and b but with c_c=2.744 Å and a space group Amma [19, 20]. As a result of the different lattice parameters of the chains and the ladders both lattices are distorted with modulated structures along their c-axis (see section III B and III C), giving rise to incommensurate modulation reflections, that can not be indexed within the space group of either structure. However, such a modulation is described within the super space group formalism [21] and the modulation reflections can be indexed by the four index notation (h, k, l, m). A reflection with the index (h, k, l, 0) is originating from the average chain structure. Contrary, a reflection with (h, k, 0, m) stems from the average ladder structure. Finally, a reflection with the mixed index (h, k, l, m) reflects the distortion of the chain and ladder lattice due to their mutual interaction. For a single reflection it is not possible to distinguish if it is due to a modulation of the chains or the ladders. The selection rules for the super space group Amma(001+γ)ss$\overline{1}$ with γ=0.6997(3), that was found for $Sr_{13.44}Bi_{0.56}Cu_{24}O_{41}$ [20], allows fundamental Bragg reflections along (0, 0, l) at $l = 2n$ with n integer for the chains and $m = 2n \sim l \cdot \sqrt{2}$ for the ladders. For the (0, 1, l)-scan only chain type Bragg reflections are allowed with $k + l = 2n$. Modulation peaks obey the rule $k + l + m = 2n$ for both types of scans. To be consistent with earlier publications on x-ray diffraction on this material the index l in the figures and in the text refers to reciprocal units of the chain lattice. If a 4-index notation is used it will be explicitly mentioned.

B. Modulation reflections at T > 200 K

To establish the modulation of the chains and ladders we performed scans along (0, 0, l) and (0, 1, l) at 270 K well above the supposed charge ordering temperature. They are shown in figure 2 and 3. The scan along (0, 0, l) shows a fundamental Bragg reflection of the chain structure at $l = 2$ and for the ladder structure at $l = 1.3976(5)$ ($m = 2$). Accordingly the ratio of the lattice parameters of chains and ladders is $\gamma = c_c/c_l = 0.6988(8)$, close to the value found for the Bi doped system [20]. Additional strong reflections are observed which can be indexed using the 4-index formalism. Their position is listed in table I together with the corresponding indices of l and m. It can be seen that all of these strong modulation peaks observed in the (0, 0, l) scan are second order reflections, either a modulation of the ladders (l=2) or of the chains (m=2). Since only second order peaks appear it is possible to distinguish between a distortion of the chains from a distortion of the ladders. For example, the reflection at l=2.601 evidences a distortion of the chain lattice. All other reflections listed for the $(0, 0, l)$-scan in table I are originating from a ladder distortion. Higher order mod-

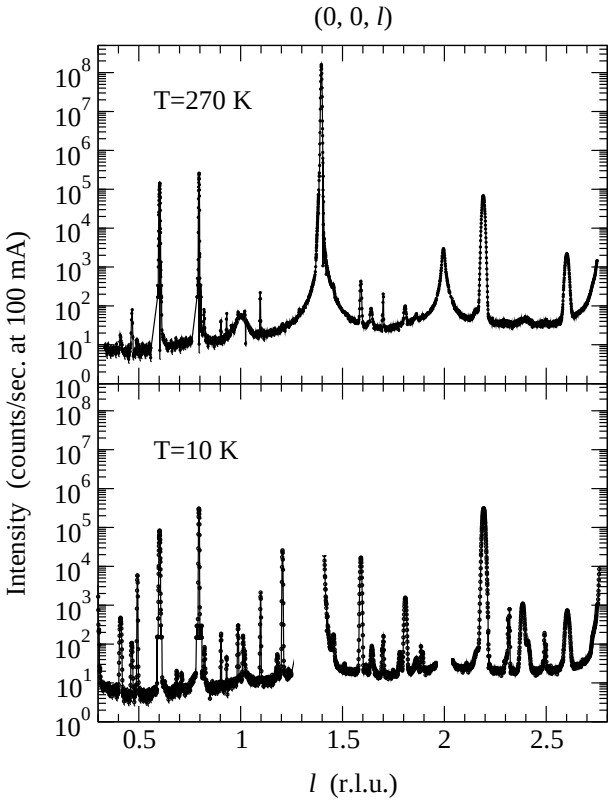

FIG. 2: Scans along (0, 0, l) at 270 K and 10 K. The position of the fundamental Bragg reflections are at l=2 for the chains and at l=1.398 for the ladders and are not shown in the scan at 10 K.

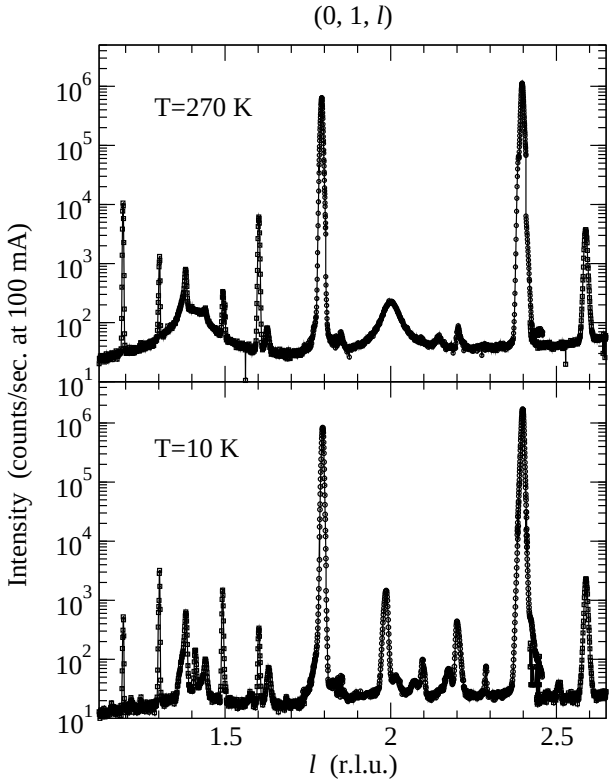

FIG. 3: Scans along (0, 1, l) at 270 K and 10 K. The position of the forbidden ladder Bragg reflection is at l=2.1, while the peaks at l=1.8 and 2.4 are first order modulation reflections. The broad reflection at l=2 at 270 K is a tail of the (0, 0, 2) Bragg peak (see text). At 10 K higher order reflections appear, e.g. at l=2 and 2.2.

ulation reflections in the $(0, 0, l)$-scan are at least three orders of magnitude smaller in intensity. The scan along (0, 1, l), shown in figure 3, exhibits strong modulation reflections and their positions are collected in table I. Here modulation reflections with indices of $l = 1$ or $l = 3$ dominate the diffraction pattern. As seen in figure 3, the first order reflections show the largest intensity about a factor of 100 smaller than the (0, 0, 1.3974) ($m = 2$) Bragg intensity. Third order reflections are about a factor 100 smaller than the first order reflections. (Also small reflections with $l = 5$ can be observed.) These reflections are first and third order modulations of the ladder structure. In general, the (0, 0, l)-scan exhibits superlattice reflections of even order, while in the (0, 1, l)-scan reflections of odd order are observed, which indicates that the phase of the modulation of neighboring layers along the b-direction is shifted by π. The small intensity of higher order reflection indicates that the modulation is of sinusoidal shape, leading only to second order reflections at (0, 0, l) and first and third order reflections for (0, 1, l). Following the considerations given in section III A and as pointed out in a recent comment [22], it becomes clear that the primary origin of all these superlattice reflections is the incommensurate modulation of the chain and ladder structure due to their different c-axis lattice parameter and not due to a charge density wave. In particular these reflections are *not* related to a five-fold superstructure, which will be discussed in more detail in section IV.

C. Modulation reflections at T < 200 K

In order to study additional distortions due to a possible charge density wave, we cooled the sample down to 10 K and repeated the scans along (0, 0, l) and (0, 1, l), as shown in the lower parts of figures 2 and 3. It is readily observed that additional superlattice reflections appear in both scans. The analysis of the position of all these additional reflections shows that they also belong to the super space group symmetry, since they can be indexed within the 4-index formalism. These additional reflections can be regarded as higher order reflections of the modulation observed at room temperature. We

(0, 0, l)	(l, m)	(0, 1, l)	(l, m)
0.602	(2,-2)	0.398*	(-1, 2)
0.796	(-2, 4)	1.192	(-3, 6)
1.397	(0, 2)	1.602	(3,-2)
2.000	(2, 0)	1.795	(-1, 4)
2.191	(-2, 6)	2.400	(1, 2)
2.601	(4,-2)	2.588	(-3, 8)
3.4*	(2, 2)	3.2*	(-1, 6)
3.6*	(-2, 8)	3.8*	(1, 4)
4.8*	(2, 4)	5.2*	(1, 6)

TABLE I: Observed reflection positions and 4-index l and m of the scans along (0, 0, l) and (0, 1, l) at 270 K. The reflections marked by a $*$ are not shown in figures 2 and 3.

(0, 0, l)	(l, m)	(0, 1, l)	(l, m)
0.410	(6,-8)	0.890*	(-4, 7)
0.493	(-3, 5)	1.110*	(6,-7)
0.987	(-6,10)	1.302	(2,-1)
1.012	(8,-10)	1.410	(7,-8)
1.098	(-1, 3)	1.493	(-2, 5)
1.205	(4,-4)	1.986	(-5,10)
1.590	(-4, 8)	2.093	(0, 3)
1.808	(6,-6)	2.205	(5,-4)
2.385	(-6,12)	2.701*	(2, 1)

TABLE II: Reflection position observed at 10 K of reflections not present or of very small intensity at 270 K.

emphasize that these additional reflections do not break the super space symmetry. In contrast to the distortion above 200 K, modulation reflections of many different orders are found and, consequently, it is impossible to determine whether the additional distortion at low temperature takes place in the chains or in the ladders. In figure 4 we compare the transverse reflection profile along k of a temperature independent reflection at (0, 0, 0.8) with a reflection that shows a strong dependence on temperature, the (0, 0, 1.2). The width of the second order reflection at (0, 0, 0.8) is resolution limited, and the lineshape is very well described by a Lorentzian scattering function

$$S(k) = \frac{A}{\left(1 - \left(\frac{k}{\Gamma_b}\right)^2\right)^y}, \qquad (1)$$

with $y = 1$, amplitude A and inverse correlation length Γ_b along the b-direction. The correlation length is then defined as $b/2\pi\Gamma_b$. In contrast, the (0, 0, 1.2) reflection shows a broadened width (see inset of figure 4) indicating a finite correlation length that we determined to about 3500 Å. In addition we find a peculiar line shape of this reflection, which is best described by a Lorentzian raised to a power of $y = 1/2$, as shown by the solid line in figure 4. Whether the presence of topological defects or the reduced dimensionality gives rise to the finite width and the

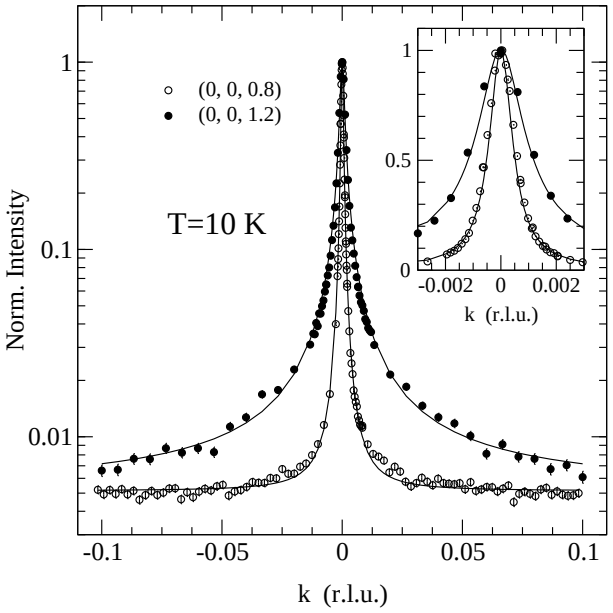

FIG. 4: Reflection profiles along the k-direction for the modulation peaks (0, 0, 0.8) and (0, 0, 1.2) on a logarithmic scale at 10 K. The peak intensity is scaled to one for both reflections. The lines are fits to a Lorentzian function for the (0, 0, 0.8) reflection and to a Lorentzian raised to a power of 1/2 for the (0, 0, 1.2) reflection. The inset shows a blow-up of the peak on a linear scale.

unusual lineshape remains an open question. Along the l-direction both reflections are resolution limited. The same lineshapes with a broadened width along the k-direction was also observed at the (0, 0, 1.8) reflection.

Turning to the temperature dependence of the modulation reflections we observe that the intensity of the first and second order modulation reflections is almost independent of temperature as can be seen in the figures 2 and 3. The difference in intensity between 10 K and 270 K is less than a factor two (see also figure 3 in ref. [14]). The higher order reflections on the other hand exhibit a very pronounced temperature dependence, some of them by several orders of magnitude between 10 K and 270 K. As an example, the reflection profiles of the (0, 0, 1.2) reflection perpendicular (k-scans) and along the chain and ladder direction (l-scan) are shown at various temperatures in figure 5. These were fitted to a Lorentzian raised to the power of $y = 1/2$ and a Gaussian profile, respectively. The fit parameters are compiled in figure 6 together with the results of the (0, 0, 1.8) reflection. The maximum intensity for both reflections has been normalized to unity. Both reflections exhibit a strong increase of their peak intensity below around 200 K and the peak intensity depends exponentially on the temperature between 100 K and 300 K (see inset of figure 6). Consistent with the absence of a reduction of the lattice symmetry, no well defined phase transition is observed. Rather a continuous cross-over into a distorted state is found. The detailed temperature dependence of

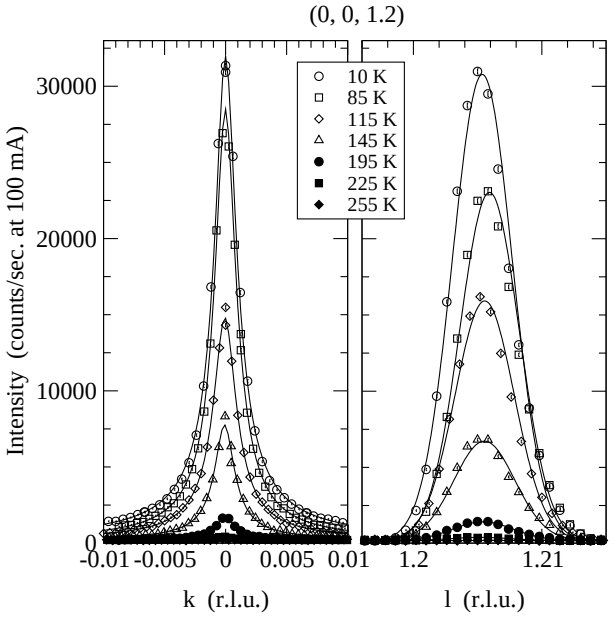

FIG. 5: Scan along k and l at the (0, 0, 1.205) reflection at selected temperature between 10 K and 255 K. The lines are fits to a Lorentzian raised to a power of 0.5 for the k-scan, and Gaussians for the l-scan.

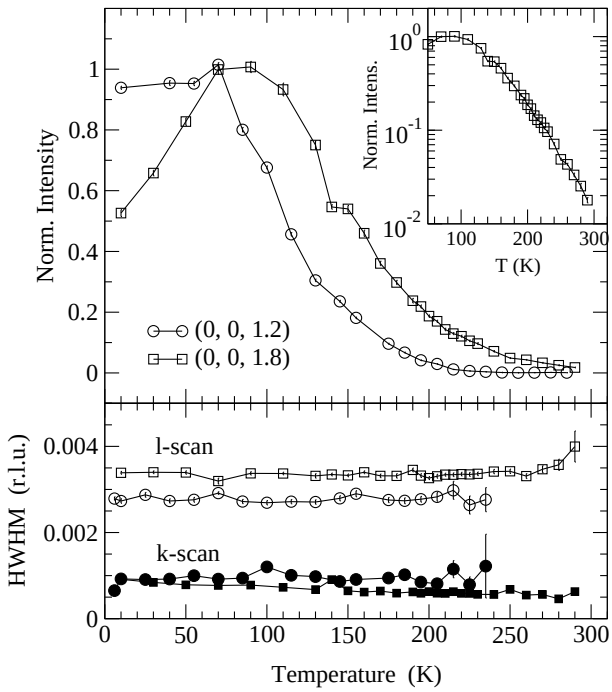

FIG. 6: Top: Temperature dependence of superlattice reflections of different orders. The maximum intensity is normalized to unity. The inset shows the intensity of the (0, 0, 1.8) reflection on a logarithmic scale. No anomaly is visible around 200 K. Bottom: Half width at half maximum along k (filled symbols) and l (open symbols).

the two reflections is very different. The (0, 0, 1.2) reflection is only observable below 250 K and shows a constant intensity below 80 K. In contrast, for the (0, 0, 1.8) reflection some residual intensity is detectable up to 280 K and below 100 K the intensity starts to decrease. As shown in the bottom part of figure 6 no variation of the peak width could be observed in the temperature regime between 10 K and 250 K for the (0, 0, 1.2) reflection. The (0, 0, 1.8) shows a slight decrease of the longitudinal peak width with increasing temperature, which could be an indication for the relaxation of lattice strain. The basically constant width indicates that the length scale of the ordering pattern is temperature independent. Neither temperature dependence could be observed in the position of these reflections, which is consistent with the fact that these modulation reflections belong to the space group symmetry and that their position is given by the mismatch of the lattice parameters of chains and ladders.

IV. DISCUSSION

The picture that emerges from the measurement of the modulation reflections is as follows: At high temperatures (270 K) both the chain and the ladder lattices are distorted with a mainly sinusoidal shape due to the mismatch of their respective c-axis lattice parameters. Accordingly, the distortion gives rise to modulation reflections of low orders, that we observe around both the ladder and the chain Bragg peaks. Thus, not only the chain lattice, but also the ladder lattice is distorted at high temperatures. At low temperatures (10 K) the modulation deviates from the sinusoidal shape leading to the appearance of higher order modulation peaks. We stress again that none of these modulations breaks the super space symmetry of the lattice. However, within each sublattice the symmetry is reduced. The variation of the modulation shape is a continuous process, as seen from the temperature dependence of the higher order modulation reflections. No well defined transition temperature can be identified from our structural studies. While the high temperature modulation with sinusoidal shape is long range ordered in all directions, the alteration of the shape at low temperature is of intermediate range order of a length scale of a few thousand Ångstrøm. The anisotropy of the peak width shows that the interactions leading to a deviation from the sinusoidal shape are stronger within a chain or ladder than the ones among subequent chains or ladders.

It is natural to associate the origin of the temperature dependent distortion with the localization of the doped holes. This is supported by the fact that the kink in the temperature dependent resistivity curve [12] coincides with the temperature were the intensity of the higher order modulation reflections starts to rise steeply. We note that the technique of hard x-ray diffraction is not sensitive to the holes itself, but to lattice distortions caused by the hole ordering. The ordering pattern of the

holes has to be such that the lattice symmetry is not broken. It is therefore most likely that the holes localize in the potential given by the incommensurate lattice distortion at high temperatures above 200 K. The localization of charge carriers distorts the lattice further and leads to a variation of the shape of the distortion, giving rise to the appearance of higher Fourier components. The amplitude and the periodicity of the high temperature distortion remains mostly unaltered. Our data show that the presence of superlattice reflections at l=2.2 and l=4.8 [23] can not be taken as evidence for a five-fold modulation of the chain lattice [14]. A five-fold modulation would result in superlattice reflection at both l=1.8 and l=2.2 which are both observed at low temperatures. However, as shown in section III the properties of the peak at l=1.8 are completely different from the ones of the l=2.2 reflection. The latter is very strong, three orders of magnitude smaller than the ladder Bragg peak at 270 K, and the intensity is independent of the temperature. In contrast, the peak at l=1.8 is very small, eight orders of magnitude smaller than the ladder Bragg peak at 270 K, and the intensity shows a very strong temperature dependence (see figure 6). This clearly demonstrates that the interpretation of these superstructure reflections in terms of a simple five-fold modulation is not possible. In particular, indexing the modulation reflection using the super space symmetry we find that the (0, 0, 1.8) reflection is a sixth order modulation of the chain lattice and also sixth order of the ladder lattice. The (0, 0, 2.2) reflection is a second order modulation reflection of the ladder lattice and similar intensities and similar temperature dependences for reflections of the same order are obtained. Not a single ordering wave vector, but a multitude of Fourier components characterizes the low temperature distortion. However, the dimer model which has already been described above may serve as a first approximation for the complicated structural modulation which takes place in the chain sublattice. In particular, inelastic neutron scattering data of $Sr_{14}Cu_{24}O_{41}$ can be described in terms of the dimer model [8, 9]. Nonetheless, we stress that the high energy x-ray diffraction experiments unambiguously reveal a much more complicated modulation in the chain and in the ladder sublattice. Since we argue that this modulation generates a pinning potential for the holes in the chains, we claim that the charge ordering pattern is more complex and may be more adequately be described by a charge density wave. This interpretation is further strenghtened by inelastic neutron scattering experiments on $La_1Sr_{13}Cu_{24}O_{41}$, which contains half doped spin chains. Although the charge carrier concentration in the chains differs considerably as compared to $Sr_{14}Cu_{24}O_{41}$, a magnetic excitation corresponding to fluctuating spin dimers has been observed in the lanthanum doped compound. This result supports our scenario of charge localization due to a pinning potential and makes a purely electronic origin of the charge and dimer ordered state very unlikely. From our present data it is not possible to construct an alternative model for the hole ordering. This would require a full structural determination, were integrated intensities of many modulation reflections are measured. It is, however, experimentally challenging to determine these for the rather diffuse reflections. Two features of our data are highly unusual, first the peculiar reflection profile perpendicular to the ladder/chain direction, that is described by a Lorentzian raised to a power of one-half, and second the exponential dependence of the intensity of the higher order reflections on the temperature. The latter feature is closely related to the temperature dependent intensity of the chain Bragg reflection whose origin is a very soft thermal mode [24]. This indicates that the hole ordering might be strongly influenced by the chain lattice dynamics and vice versa.

V. CONCLUDING SUMMARY

We have reported on the incommensurate lattice distortions in $Sr_{14}Cu_{24}O_{41}$ and shown that the crystal structure of this composite system exhibits a strong mostly temperature independent lattice distortion due to the incommensurate ratio of the lattice parameters of the chains and the ladders, respectively. Upon cooling the sample to 10 K, additional modulation reflections appear, that can be described as higher order reflections of the distortion present at room temperature. These low temperature reflections indicate a variation of the shape of the distortion pattern due to the localization of holes. It is found that holes localize in the lattice potential given by the high temperature distortion, since the periodicity of the modulation is not affected by the charge localization.

VI. ACKNOWLEDGMENT

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